Ph.D. Synopsis submitted to

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Preparation and Characterization of $NiFe_2O_4$ and $CoFe_2O_4$ Thin Films for Electrochemical Supercapacitor Applications

Abstract of proposed work plan/problem:

In the present research work; $NiFe_2O_4$ and $CoFe_2O_4$ thin films will be deposited onto amorphous and conducting glass substrates from salts of nickel and cobalt by simple and inexpensive chemical **Spray Pyrolysis Technique**. Structural, morphological, optical, electrical and electrochemical properties of the as deposited $NiFe_2O_4$ and $CoFe_2O_4$ thin films will be studied by using XRD, SEM, FESEM, UV spectrophotometer, DC electrical conductivity measurement, cyclic voltammetry and galvanostatic charge/discharge measurements.

1. Introduction:

Thin film studies have directly or indirectly advanced many new research areas in material science which are based on phenomena uniquely characterizing the thickness, geometry, and structure of the films. Due to the exhaustion of natural resources and associated environmental issues and increasing global energy demand for future portable devices and electric vehicles, there has been an intense interest in alternative energy conversion and storage systems with high efficiency, low cost and environmental kindliness. Supercapacitors, also known as electrochemical capacitors, are kind of promising energy storage devices because of their high power density, fast charging/discharging rate and excellent cycle stability. Such outstanding properties make them promising in a wide range of applications from hybrid vehicles and portable electronics to military devices, where high power density and long cycle-life are highly desirable. However, their commercial applications have been limited due to lower energy density and higher cost.

Supercapacitors storage energy in either capacitive (double layer of electrostatic charges) or pseudo-capacitive (a faradaic battery like reaction) nature. Supercapacitors exploit both the advantages of battery (high energy density) and conventional dielectric capacitors (high power density). Supercapacitors easily offer high specific capacitance value up to several thousand farads for applications. Supercapacitor can be divided into two groups EDLC (Electrochemical

Double Layer Capacitors) and Pseudocapacitors. The capacitance of EDLC arises from the charge separation at the interface between the electrode and electrolyte. In case of pseudocapacitors the specific capacitance arises from the faradaic reactions occurring at the electrode material. The interest using pseudocapacitors based materials for electrochemical capacitor is that the energy density associated with faradaic reaction is much higher than traditional double layer capacitance [1].

The transition material oxides such as ruthenium oxide, manganese oxide, iron oxide, tin oxide, nickel oxide, indium oxide, bismuth oxide, vanadium oxide, bismuth iron oxide, nickel ferrite, iridium oxide, perovskites, ferrites etc are widely used as electrode material for pseudocapacitors because of their fast reversible faradaic reaction. Metal oxide materials provide high energy density for pseudocapacitors, due to high surface area with good electrical conductivity [2].

Due to the above mentioned advantages and applications of metal oxides; it is proposed to prepare $NiFe_2O_4$ and $CoFe_2O_4$ thin films by simple and inexpensive chemical spray pyrolysis method. These films will be used as electrode in electrochemical supercapacitors.

2. Review of literature and development in the subject (Previous work done in the relevant area):

In literature, so far, various metal oxide nanostructures including RuO_2, V_2O_5, Bi_2O_3, IrO_2 have been employed as efficient pseudocapacitors. However, these materials are expensive and therefore, are not commercially viable. Thereby, searching for alternate eco-friendly and economical supercapacitive materials with high yield is a major subject in this field. Ferrites can be one of the promising candidates because they are inexpensive, abundant and environmentally benign.

Zate and coworkers [3] studied the electrochemical supercapacitive properties of sprayed nickel ferrite thin film electrodes deposited onto stainless-steel substrate. The X-ray diffraction and scanning electron microscopy measurements were used for the structural elucidation and the morphological evolution studies, respectively. Nickel ferrite thin films demonstrated the maximum specific capacitance of 202 Fg^{-1} (at 2 $mAcm^{-2}$). Cyclic-voltammetry curve shape of nickel ferrite electrode in Na_2SO_3 electrolyte was nonsymmetrical with a very good electrochemical life cycle.

T. Shanmugavel et al. [4] synthesized nanocrystalline forms of nickel ferrite ($NiFe_2O_4$) with the aid of single step chemical combustion method using citric acid. The single phase formation of nickel ferrite was confirmed through powder X-ray diffraction (XRD). The presence of various functional groups was confirmed through Fourier transform infrared spectroscopic (FTIR) analysis and the compositional analysis was performed through Energy dispersive X-ray studies (EDX). The microstructural, surface morphological properties of $NiFe_2O_4$ were also investigated.

M. Khairy and his colleagues [5] prepared polyaniline-$NiFe_2O_4$ nanocomposites (PANI-$NiFe_2O_4$) with different contents of $NiFe_2O_4$ (2.5, 5 and 50 wt%) chemical oxidation polymerization. The prepared samples were characterized using some techniques such as FTIR, X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermo gravimetric analysis (TGA). FTIR spectra revealed to the formation of some interactions between the PANI macromolecule and the $NiFe_2O_4$ nanoparticles, while the thermal analyses indicated an increase in the composites stability for samples with higher $NiFe_2O_4$ nanoparticles contents.

P. Samarasekara et al. [6] synthesized $Fe_xNi_yO_z$ films using spin coating method. The film samples were characterized using EXAFS. Peaks of Fourier transform of EXAFS could be observed at 1.4, 2.5 and 3.0 Å without phase factor correction for Fe-O, Fe-Fe and Ni-Ni bonds, respectively for sample fabricated at 900 rev/m for 2 min and annealed at 500ºC for 3 hours. Owing to unpaired electrons in outer shell of Fe and Ni atoms, Fe and Ni mixed thin films are considered to be prime candidates of magnetic devices.

Gagan Dixit and coworkers [7] reported structural, morphological, magnetic and optical properties of nickel ferrite thin films with different film thicknesses. All the films were deposited on Si (100) substrate by pulsed laser deposition technique. Thicknesses of the films were determined by x-ray reflectivity. These films were characterized by X-ray diffractogram, FTIR and Raman spectroscopy for structural and phase confirmation. FTIR and Raman spectra confirmed mixed spinel nature of nickel ferrite. The results were explained on the basis of anisotropy induced by cation inversion and strain. Optical properties were studied by UV-Vis reflectance spectra. The value of optical band gap (5.7eV) was found to be independent of film thickness.

Georgiana Dascalu et al. [8] synthesized $CoFe_2O_4$ in bulk and thin film form by using pulsed laser deposition. It is observed that the insertion of different elements in the cobalt ferrite

spinel structure can drastically change the electric and magnetic characteristics. The structural characteristics and chemical composition of the samples were investigated using profilometry, Raman spectroscopy, X-Ray diffraction measurements and ToF-SIMS analysis. It was observed that cobalt ferrite thin films show a single spinel structure.

V.S. Kumbhar et al. [9] prepared cobalt ferrite ($CoFe_2O_4$) thin films on stainless steel substrate by simple chemical route from an alkaline bath containing Co^{2+} and Fe^{2+} ions. The films are characterized for structural, surface morphological and FTIR properties. The XRD and FTIR studies revealed formation of single phase of $CoFe_2O_4$. The formation of nano-flakes like morphology was observed from scanning electron microscope. The electrochemical behavior of $CoFe_2O_4$ film has been studied using cyclic voltammetry in 1M NaOH electrolyte. The maximum specific capacitance of 366 Fg^{-1} is obtained at the scan rate of 5 mVs^{-1}.

Cameliu Himcinschi and coworkers [10] deposited structures of nickel and cobalt ferrites on Nb doped $SrTiO_3$ by pulsed laser deposition. X-Ray diffraction and atomic force microscopy showed that the films have a good crystalline quality and smooth surfaces. A large number of phonon bands were observed in the polarization dependent Raman spectra of the ferrite films than expected for the cubic spinel structures. The diagonal components of the dielectric function for nickel and cobalt ferrites are determined from ellipsometry in the 0.73-5 eV photon energy range. The absorption edge was analyzed using a bandgap model and the energies for the indirect and direct optical transitions were calculated. It was found that both nickel and cobalt ferrites have indirect bandgaps of 1.65 eV and 1.42 eV, respectively.

Razia Nongjai et al. [11] deposited thin films of cobalt ferrite was deposited on Si (1 0 0) substrate using pulsed laser deposition (PLD) technique. The deposited films were characterized by X–ray Diffraction (XRD), X–ray reflectivity (XRR), Rutherford Backscattering Spectroscopy (RBS) and Raman Spectroscopy and were found to be single phase, textured along (1 1 1) directions and approximately matching the stoichiometry of the target with negligible strain. The films had a very uniform and flat surface. Raman spectroscopy measurement confirmed the formation of single phase cubic spinel structure.

3. Objectives of Research/Proposed Hypothesis:

Following are the objectives of present research work for the Ph. D topic.

1. To prepare good quality $NiFe_2O_4$ and $CoFe_2O_4$ thin films by chemical spray pyrolysis technique by optimizing various preparative parameters.

2. To characterize $NiFe_2O_4$ and $CoFe_2O_4$ thin films for physical properties like structural, morphological, optical and electrical measurement.

3. To study the supercapacitive behavior of $NiFe_2O_4$ and $CoFe_2O_4$ thin films by using cyclic voltammetry, galvanostatic charge/discharge technique and Nyquist analysis.

4. Methodology to be adopted:

Metal oxide thin films can be prepared by many deposition methods mainly physical and chemical methods. Physical methods have certain drawbacks and difficulties. For metal oxide thin films, chemical methods are useful because chemical methods are relatively economical and easier ones as compared to physical methods. Chemical methods are classified as gas phase and liquid phase. In liquid phase chemical methods include spray pyrolysis, electrodeposition, chemical bath deposition, successive ionic layer adsorption and liquid phase epitaxy etc.

Of all these methods available for deposition of metal oxide thin films, spray pyrolysis is a simple and low cost method for the preparation of metal oxide thin films for electrochemical supercapacitors. The advantages of spray pyrolysis are:

- Ability to produce large area high quality adherent thin films of uniform thickness;
- Does not require vacuum at any stage;
- The deposition rate and the thickness of the film can be easily controlled over a wide range by changing spray parameters; and
- Major advantage of this method is operating at moderate temperature (100-500°C)

In our present research work, $NiFe_2O_4$ and $CoFe_2O_4$ thin films will be prepared by chemical spray pyrolysis method and properties of deposited films such as structural, morphological, compositional, optical, electrical and electrochemical characteristics will be studied.

a) Preparation of $NiFe_2O_4$ and $CoFe_2O_4$ Thin Films.

It is proposed to prepare $NiFe_2O_4$ and $CoFe_2O_4$ thin films by chemical spray pyrolysis. At initial stages the efforts will be done in order to deposit good quality $NiFe_2O_4$ and $CoFe_2O_4$ thin

films on glass and FTO coated conducting glass substrates. The various preparative parameters like concentration of precursor solution, thickness, substrate temperature and other parameters will be optimized to get good quality $NiFe_2O_4$ and $CoFe_2O_4$ thin films. The as deposited films will be characterized by various characterization techniques

b) Structural Studies:

The as deposited $NiFe_2O_4$ and $CoFe_2O_4$ thin films will be characterized by X-Ray Diffraction (XRD) technique. The crystal structure, interplanar spacing, lattice planes, lattice constants and crystallite size will be obtained and correlated with the film properties.

c) Morphological and Compositional Studies:

The morphology of the prepared $NiFe_2O_4$ and $CoFe_2O_4$ thin films will be studied by using Scanning Electron Microscopy (SEM) or Atomic Force Microscopy (AFM). The grain size, surface roughness, porosity will be studied using SEM and AFM techniques. The compositional analysis of as deposited $NiFe_2O_4$ and $CoFe_2O_4$ thin films will be studied by using Energy Dispersive Analysis by X–Rays (EDAX) technique. The correlation between as taken composition and film composition will be obtained.

d) Optical Studies:

The optical absorption of $NiFe_2O_4$ and $CoFe_2O_4$ thin films will be obtained by using UV–Vis (Ultra Violet–Visible) spectrophotometer. The coefficient of absorption, band gap energy (Eg), nature of transition, power factor will be obtained from optical absorption spectra.

e) Electrical Studies:

The electrical conductivity measurements of as deposited $NiFe_2O_4$ and $CoFe_2O_4$ thin films will be carried out by using DC two point probe method. The room temperature conductivity, activation energy will be obtained and correlated with film properties.

f) Electrochemical Supercapacitor Studies:

Performance of $NiFe_2O_4$ and $CoFe_2O_4$ thin films in supercapacitor will be evaluated with respect to various parameters such as scan rate, specific capacitance, stability cycles and potential range. The supercapacitive performance of $NiFe_2O_4$ and $CoFe_2O_4$ thin films will be tested for symmetric and asymmetric modes, for achieving high power density. The charge-discharge mechanism will be studied using chronopotentiometry and the parameters such as average capacitance, coulomb efficiency, specific energy, and specific power will be calculated.

The purpose of present research work is to improve pseudo-capacitive properties such as specific power, specific energy and coulomb efficiency of $NiFe_2O_4$ and $CoFe_2O_4$ thin films by using simple and cost effective spray pyrolysis method.

5. Importance of the study/Society application:

Thin film based supercapacitors exhibited superior values compared to their bulk and composites of electrodes. The market demand is to produce supercapacitor with high specific capacitance, high energy density and good cyclic stability. Now a day's the performance of ternary metal oxide thin film based supercapacitor is sufficient for certain applications than binary composites. $NiFe_2O_4$ and $CoFe_2O_4$ thin film material is easily available, low cost and shows good faradaic reaction. Among various metal oxides materials of ruthenium oxide shows good specific capacitance, long cyclic stability and high energy density but ruthenium oxide is costly, not easily available and not environment friendly. To overcome the drawback of ruthenium oxide, $NiFe_2O_4$ and $CoFe_2O_4$ materials can be used for supercapacitor applications with high specific capacitance, high conductivity, better charge/discharge rate and low cost. By considering above view, $NiFe_2O_4$ and $CoFe_2O_4$ films will be studied thoroughly in the present work for societal applications like supercapacitors.

6. Proposed Work Plan/ Formulation and Structure of Study:

Plan of work and targets to be achieved during First Year:

A through literature survey and collection of papers will be done in order to get more and deep information about work already done and scope of the present work. The literature includes collection of Journals, Books and some research papers related to the present work. Various chemicals will be procured and efforts will be done to deposit good quality $NiFe_2O_4$ and $CoFe_2O_4$ thin films. Two progress reports will be submitted at the end of this year.

Plan of work and targets to be achieved during Second Year:

During second year, all preparative parameters will be optimized in order to get good porous $NiFe_2O_4$ and $CoFe_2O_4$ thin films. All deposited films will be characterized by various techniques such as XRD, SEM, FESEM, TEM, EDAX, UV–Vis, and DC electrical conductivity. The Performance of $NiFe_2O_4$ and $CoFe_2O_4$ thin films in supercapacitor will be evaluated with respect to various parameters such as scan rate, specific capacitance, stability cycles and

potential range. The charge-discharge mechanism will be studied using chronopotentiometry and the parameters such as average capacitance, coulomb efficiency, specific energy and specific power will be calculated. Also we will try to submit two or more research papers to reputed international research journals. Two progress reports will be submitted at the end of this year.

Plan of work and targets to be achieved during Third Year:

Results obtained in second year will be analyzed and published in reputed journals. Also the outcomes of our research work will be presented in national and international gatherings such as Seminars, Workshops, and Conferences etc during this year. Once this is done final synopsis will be submitted and after this thesis will be written. Thesis will be submitted to the university.

7. References

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